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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

10/520249
Rec'd PCT/PTO 04 JAN 2005
01 NOV 2004
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Applicant's or agent's file reference RPW:JL:FP17980	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International Application No. PCT/AU2003/000864	International Filing Date (day/month/year) 4 July 2003	Priority Date (day/month/year) 5 July 2002
International Patent Classification (IPC) or national classification and IPC Int. Cl. ⁷ : C01C 3/08, 3/11; G02B 1/00, 1/02; H01L 21/58, 23/14, 41/16; H01S 3/16, C07C 211/62, 211/63		
Applicant THE UNIVERSITY OF SYDNEY et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 5 sheet(s).

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 16 January 2004	Date of completion of the report 13 October 2004
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I. Basis of the report**1. With regard to the elements of the international application:***

- ☐ the international application as originally filed.
- ☒ the description, pages **1-10, 12-19, 21-51** as originally filed,
pages , filed with the demand,
pages **11, 20** received on **9 September 2004** with the letter of **9 September 2004**
- ☒ the claims, pages **52-55, 58-60, 62** as originally filed,
pages , as amended (together with any statement) under Article 19,
pages , filed with the demand,
pages **56-57, 61** received on **9 September 2004** with the letter of **9 September 2004**
- ☒ the drawings, pages **1/31 – 31/31**, as originally filed,
pages , filed with the demand,
pages , received on with the letter of
- ☐ the sequence listing part of the description:
pages , as originally filed
pages , filed with the demand
pages , received on with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/fig.

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1-31, 34-53	YES
	Claims 32-33	NO
Inventive step (IS)	Claims 1-31, 34-53	YES
	Claims 32-33	NO
Industrial applicability (IA)	Claims 1-53	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)

The present application appears directed to a method for controlling thermal expansion behaviour of materials and where these materials are used in devices in which the thermal expansion behaviour is anomalous (ie can be either zero thermal expansion (ZTE), negative thermal expansion (NTE) or positive thermal expansion (PTE)).

The problem to solve appears to reside in providing a method that controls the thermal expansion behaviour of materials used in a wide array of devices such that the device operates more reliably and is dimensionally stable over broader temperature ranges/ fluctuations.

The following documents are considered relevant to the present invention;

D1 - R. H Baughman, "Negative thermal expansion..." (1973)

D2 - US 4255535 A

D1 discloses molecular processes contributing to NTE for mainly linear crystalline polymers (ie CC 'bridging'). The thermal expansion is identified by modelling the torsional motion (thus creating a torsional *vibrational* amplitude) of polymer chains with respect to dimensional changes resulting from said motion. Page 2977 (top of column 2) further discloses a thermal expansion coefficient less than $-9 \times 10^{-6} \text{K}^{-1}$ for polyethylene crystals which are derived from the rotation of CC bonds with an increase in temperature (20-120°C). D1 does not disclose the presence of two different atoms either side of the bridge nor does D1 directly prescribe transverse vibrational modes to control the thermal expansion behaviour of the crystalline polymers. Additionally, D1 also does not indicate whether a single crystal of an anisotropic material directs the thermal expansion of said crystalline polymers. See abstract, pages 2977-2983.

D2 discloses polymeric composites having near-zero, negative or positive thermal expansion coefficients along at least one axis. The composites are useful in applications where the substantial elimination of dimensional instability in a structural element is highly desirous. The composite comprises substantially polyacetylene (CC 'bridging' - see Col 7, L50-55) and said expansion coefficient is calculated as an absolute value of $< 1.0 \times 10^{-6} \text{C}^{-1}$ (Col 2-3) along at least one axis. The thermal expansion behaviour of said polymer composite is suitably identified as being a result of chain conformational fluctuations and chain misalignments incurred through phase transitions of molecules in the thermal processing techniques described therein (Cols 7-8). These aspects are considered to 'control' the thermal expansion behaviour of said polymer composites - see also Cols 12-13. However D2 makes no disclosure to the presence of two different atoms either side of the diatomic or multi-atomic bridge. There is also no mention of the polymeric composites containing a single crystal of an anisotropic material that directs thermal expansion due to its alignment in said polymeric composites. Furthermore D2 does not directly disclose transverse vibrational modes controlling the thermal expansion behaviour of the acetylenic polymers.

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of**NOVELTY (N) Claims 32-33**

Independent claim 32 merely defines controlling the thermal expansion behaviour of any material by incorporating any component having a thermal expansion coefficient less than $-9 \times 10^{-6} \text{K}^{-1}$. The method to control thermal expansion behaviour of said material is not restricted to the methods espoused in the other independent claims (claims 1, 29, 35, 42 and 51). As such it is considered the subject matter of present claims 32-33 is singularly disclosed in D1 and D2. See also the comments made in Box VIII regarding the viability of claim 32.

INVENTIVE STEP (IS) Claims 32-33

Since D1-D2 anticipate the features contained in present claims 32-33, accordingly these claims are thought to also lack an inventive step in light of the cited references.

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

1. The description does not fully support claim 32 of the present invention because the component defined therein can be any component possessing a thermal expansion coefficient of less than $-9 \times 10^{-6} \text{ K}^{-1}$. The method to control the thermal expansion behaviour of said material is only defined by the component being incorporated into said material and not through the mechanism of vibrational modes as being claimed in the other independent claims. Furthermore the method of present claim 32 appears to encompass any method of controlling thermal expansion behaviour of a material.

The description frequently describes components requiring specific characteristics, those including at least 1 diatomic bridge, which are further characterised by having at least one vibrational mode causing atoms either side of said bridge to move together to a similar or greater extent than competing vibrational modes causing the atoms either side of said bridge to be moved apart (ie ZTE or NTE) in order to effect the material working of the present invention. The description at p9 (L3-7) categorically states "*Only components of the present invention have been able to achieve such a considerable extent of NTE.*". Furthermore the description at pages 48-49 also reinforce the notion that incorporating components with diatomic bridges, having at least one transverse vibrational mode, was typically the cause of NTE in the materials described by the current application.

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electronics device; a thermal transfer device; a zero
insertion force socket; a component for a superconductor,
high precision instrument or frequency resonator; an
optical device displaying birefringence or that is
5 optically transparent; an interference device;
or the device can display: piezoelectric properties;
optical activity; or nonlinear optical properties.

Advantageously all of these devices can thus be
provided with controllable thermal expansion behaviour,
10 making the devices more reliable and dimensionally stable
in use over broader temperature ranges/fluctuations.

In a further unique aspect the present invention
provides a method for directing the thermal expansion
behaviour of a material, and a material produced by this
15 method. The method comprises the step of incorporating
into the material a component including one or more
diatomic bridges, the or each bridge extending between two
atoms in the component, with the or each diatomic bridge
having at least one vibrational mode that causes the two
20 atoms on either side of the bridge to be moved together to
a similar or greater extent than competing vibrational
mode(s) that cause the two atoms on either side of the
bridge to be moved apart, characterised in that the
component comprises a single crystal of an anisotropic
25 material that, by virtue of its alignment in the material,
directs thermal expansion (ie. anisotropically).

Preferably the component comprises a portion or the
entirety of the material.

This unique aspect of the invention can incorporate
30 some of the preferred features of the first, second, third
and fourth aspects of the invention as appropriate.

Brief Description of the Drawings

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typically, though not always, by "infinite" molecular coordination networks (for example, where the diatomic bridge is present throughout the material). Further, composites including two or more of these materials (or one of these materials and an unrelated material) were produced.

Material Examples:

(a) Materials based on the $\text{Zn}(\text{CN})_2$ -type or $2 \times (6,4)$ cubic structure (doubly interpenetrating diamond-type nets). Variations included substitution of divalent metals for some or all of the Zn atoms. Such divalent metal ions included $\text{Cd}(\text{II})$, $\text{Hg}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Be}(\text{II})$, $\text{Mg}(\text{II})$, $\text{Pb}(\text{II})$ and $\text{Co}(\text{II})$. Variations also included substitution of mixtures of univalent, divalent and trivalent metal ions for Zn to give materials of the form:

$$\{(\text{M1}_1^{\text{I}})_{x_1}(\text{M1}_2^{\text{II}})_{x_2} \dots (\text{M1}_n^{\text{II}})_{x_n}\} \{(\text{M2}_1^{\text{I}})(\text{M3}_1^{\text{III}})\}_{y_1} \{(\text{M2}_2^{\text{I}})(\text{M3}_2^{\text{III}})\}_{y_2} \dots \{(\text{M2}_m^{\text{I}})(\text{M3}_m^{\text{III}})\}_{y_m} (\text{CN})_2$$

where M1_i included $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Hg}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Be}(\text{II})$, $\text{Mg}(\text{II})$, $\text{Pb}(\text{II})$ and $\text{Co}(\text{II})$; M2_i included $\text{Li}(\text{I})$ and $\text{Cu}(\text{I})$; M3_i included $\text{Al}(\text{III})$, $\text{Ga}(\text{III})$ and $\text{In}(\text{III})$; n and m being any non-negative whole numbers with at least one greater than or equal to unity; and $(x_1 + x_2 + \dots + x_n) + 2 \times (y_1 + y_2 + \dots + y_m) = 1$. Examples of this class included $\text{Zn}(\text{CN})_2$, $\text{Zn}_{0.8}\text{Cd}_{0.2}(\text{CN})_2$, $\text{Zn}_{0.64}\text{Cd}_{0.36}(\text{CN})_2$, $\text{Cd}(\text{CN})_2$, $\text{Mn}(\text{CN})_2$, $\text{Zn}_{0.5}\text{Hg}_{0.5}(\text{CN})_2$, $\text{Li}_{0.5}\text{Ga}_{0.5}(\text{CN})_2$ and $\text{Cu}_{0.5}\text{Al}_{0.5}(\text{CN})_2$.

(b) Materials of the general formula given in (a) above but with a single diamond-type network rather than two interpenetrating networks, optionally with counterions or molecules incorporated into the structure. Incorporation of counterions into the interstitial cavities required an appropriate inclusion of lower- or higher-valent metals into the network lattice. Examples of this class included $\text{Cd}(\text{CN})_2 \cdot \frac{1}{2} \text{CCl}_4$, $[\text{NMe}_4]_{0.5} [\text{Cu}^{0.5}\text{Zn}^{0.5}(\text{CN})_2]$, $\text{Cd}(\text{CN})_2 \cdot \text{CMe}_4$,

33. A method as claimed in claim 32 wherein the component has a coefficient of thermal expansion that ranges from: $-9 \times 10^{-6} \text{ K}^{-1}$ to $-21 \times 10^{-6} \text{ K}^{-1}$ in all directions; or $-15 \times 10^{-6} \text{ K}^{-1}$ to $-62 \times 10^{-6} \text{ K}^{-1}$ along any one direction.

5 34. A method as claimed in claim 32 or 33 that is otherwise as defined in any one of claims 1 to 30.

35. A method for altering the thermal expansion behaviour of a material that comprises a component having a plurality of diatomic bridges, each bridge extending
10 between two atoms in the component and having at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart,
15 the method comprising the step of incorporating into the component two or more different atoms such that, for at least some of the diatomic bridges, the two atoms on either side of the bridge are different.

36. A method as claimed in claim 35 wherein the thermal
20 expansion is tunable by varying the relative ratios between the two or more different atoms on either side of the diatomic bridge.

37. A method as claimed in claim 35 or 36 wherein the two atoms on either side of the bridge are different metals,
25 semi-metals or non-metals, or combinations thereof.

38. A method for controlling the thermal expansion behaviour of a material substantially as herein described with reference to the Examples and/or the accompanying drawings.

30 39. A material produced by the method of any one of the preceding claims.

40. A material as claimed in claim 39 comprising one or more of:

(a) materials based on the Zn(CN)_2 -type or $2x(6,4)$ cubic structure (doubly interpenetrating diamond nets), optionally including substitution of divalent metals for some or all of the Zn atoms, including Cd(II), Hg(II), Mn(II), Be(II), Mg(II), Pb(II) and Co(II), and optionally comprising substitution of mixtures of univalent, and optionally divalent and trivalent metal ions for Zn to give materials of the form:

$$\{ (M1_1^{II})_{x_1} (M1_2^{II})_{x_2} \dots (M1_n^{II})_{x_n} \} \{ (M2_1^{I}) (M3_1^{III}) \}_{y_1} \{ (M2_2^{I}) (M3_2^{III}) \}_{y_2} \dots$$

$\{ (M2_m^{I}) (M3_m^{III}) \}_{y_m} (\text{CN})_z$, where $M1_i$ includes Zn(II), Cd(II), Hg(II), Mn(II), Be(II), Mg(II), Pb(II) and Co(II); $M2_i$ includes Li(I) and Cu(I); $M3_k$ includes Al(III), Ga(III) and In(III); n and m being any non-negative whole numbers with at least one greater than or equal to unity; and $(x_1 + x_2 + \dots + x_n) + 2 \times (y_1 + y_2 + \dots + y_m) = 1$;

(b) materials of (a) but with a single diamond-type network rather than two interpenetrating networks, optionally with other ions or molecules incorporated into the structure, optionally with the inclusion of lower- or higher-valent metals into the network lattice;

(c) materials of (a) and (b) but with more than two interpenetrating diamond networks;

(d) materials based on Ga(CN)_3 -type structure, optionally satisfying the general formula:

$$\{ (M1_1^{III})_{x_1} (M1_2^{III})_{x_2} \dots (M1_n^{III})_{x_n} \} \{ (M2_1^{II}) (M3_1^{IV}) \}_{y_1} \{ (M2_2^{II}) (M3_2^{IV}) \}_{y_2} \dots \{ (M2_m^{II}) (M3_m^{IV}) \}_{y_m} (\text{CN})_z$$

, where $M1$ includes trivalent metal ions including Fe(III), Co(III), Cr(III), Ti(III), Al(III), Ir(III), Ga(III), In(III) and Sc(III); $M2$ includes divalent metal ions including Mg(II), Zn(II), Cd(II), Co(II), Fe(II), Ru(II), Mn(II) and Ni(II); $M3$ includes tetravalent metal ions such as Pd(IV) and Pt(IV); n and m being non-negative whole numbers with at least one greater

48. A composite as claimed in claim 47 further comprising a binding agent for the material and unrelated material.

49. A device formed from or comprising material having controllable thermal expansion behaviour, the material
5 being produced by a method as claimed in any one of claims 1 to 38, or being as claimed in any one of claims 40 to 48.

50. A device as claimed in claim 49 that is: an optical fibre; a laser; an optical, electronics or thermal
10 electronics component; a substrate or support for an optical component, electronics device or thermal electronics device; a thermal transfer device; a zero insertion force socket; a component for a superconductor, high precision instrument or frequency resonator; an
15 optical device displaying birefringence or that is optically transparent; an interference device; or a device that displays: piezoelectric properties; optical activity; or nonlinear optical properties.

51. A method for directing the thermal expansion behaviour
20 of a material comprising the step of incorporating into the material a component including one or more diatomic bridges, the or each bridge extending between two atoms in the component, with the or each diatomic bridge having at least one vibrational mode that causes the two atoms on
25 either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart, characterised in that the component comprises a single crystal of an anisotropic
30 material that, by virtue of its alignment in the material, directs thermal expansion.

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